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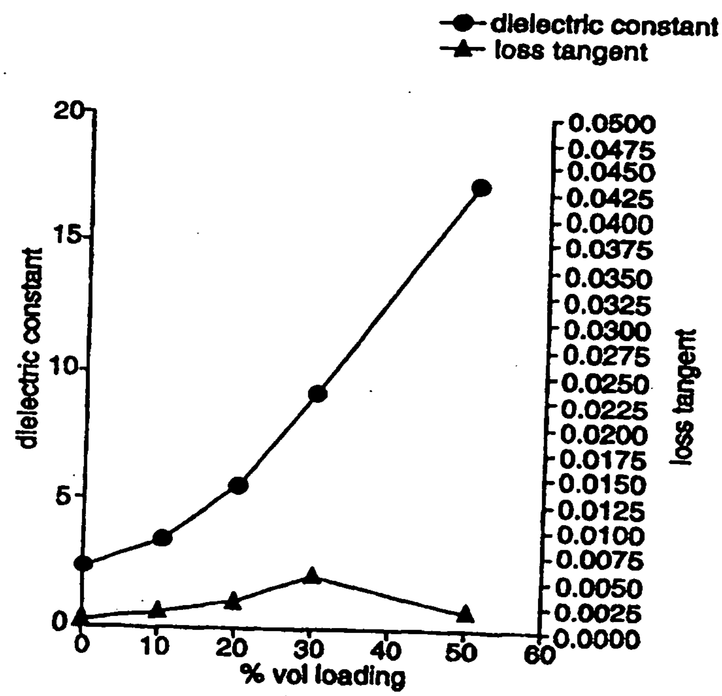
(57) Abstract

A thermoplastic elastomer which may be formulated to have a wide range of dielectric properties as required for a particular application. The material of the invention is preferably provided in the form of a film, which may be bonded to metallic layers, additional dielectric layers, or other circuit structures to form a laminate structure with the desired dielectric properties.



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THERMOPLASTIC ELASTOMERIC SUBSTRATE MATERIAL WITH TUNABLE DIELECTRIC PROPERTIES AND LAMINATES THEREOF

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a substrate or laminate which may be used as a mount for electronic devices. More particularly, the present invention is a thermoplastic elastomeric substrate or laminate material with tunable dielectric properties. Even more particularly, the present invention is a thermoplastic elastomer, preferably having a low dielectric loss, which may be formulated to have a wide range of dielectric constants as required for a particular application. The thermoplastic elastomer material of the invention, which preferably has a thermoplastic polymeric component comprising polypropylene and an elastomeric component comprising ethylene-propylene-diene monomer (EPDM), preferably has a loss tangent of less than about 0.005, most preferably less than about 0.003, and may be provided as a film or as a laminate structure.

Description of Related Art

Many substrate materials with particular electrical properties for the mounting of electronic devices are well known in the art, and are used widely in many different types of electronic devices. For example, laminates serve predominantly as substrates for printed circuits and the like and are conventionally made up of resin-impregnated sheets which are cut into leaves or panels and superimposed into layers. The layers are placed under heat and pressure and joined to form a solid unit. The resulting laminates can be covered on one or both sides by laminating with a metallic material, or can be provided with metal layers by well-known deposition methods.

A wide range of polymeric materials are used as substrate or laminate elements in electronics applications, and a great deal of information regarding their properties is known. See, for example, Brydson, Plastics Materials, 4th ed., 1985, at pages 100-110. These polymeric materials are electrical insulators, i.e. they

may withstand a potential difference between different points of a given piece of material with the passage of only a small electric current and a low dissipation energy. In certain applications the influence of a polymeric material on the capacitance of a condenser, known as its dielectric constant, becomes particularly important. The dielectric constant of a material, ε_r, is defined as the ratio of the condenser capacity, using the given material as a dielectric, to the capacity of the same condenser without the dielectric.

When a polymeric material is placed in an electric field, its dielectric constant depends on both electronic polarization effects within its molecular structure and on dipole polarization effects with neighboring molecules. Therefore, a symmetrical or non-polar molecule, which experiences only electronic polarization effects, will have a lower dielectric constant than a polar molecule, which is under the influence of both electronic and dipole polarization effects. Since dipole polarization involves movement of part or even the whole of the molecule, the dielectric constant of polar molecules will depend on the "internal viscosity", i.e. the out of step motions of the dipoles, in the material.

This internal viscosity also produces dielectric power losses at certain frequencies when the dielectric material is placed in an alternating electric field. These losses are measured as the fraction of energy absorbed per cycle by the dielectric from the electric field. The power factor and the dissipation factor arise by considering the delay between the changes in the field and the change in polarization, which in turn leads to a current in a condenser leading the voltage across it when a dielectric is present. The angle of lead is referred to as the phase angle θ, while the term $90-\theta$ is known as the loss angle, δ. The dissipation factor, or loss tangent, for a particular material is $\tan \delta$.

An important first step in the design of any electronic device which will absorb or transmit energy is the selection of an appropriate dielectric substrate material. There is no one ideal substrate, and the material selected depends on the properties required for the intended application. The most important properties of a particular material are its dielectric constant (ε_r) and loss tangent ($\tan \delta$) in the selected temperature and frequency range over which the device will operate.

Generally, a low loss tangent suggests excellent energy transmittance, and such materials are useful in the design of electronic devices such as antennas. Conversely, a microwave or radar absorber may require a dielectric material with a much higher loss tangent. Low frequency, low loss applications, such as tapered slot antennas, require a material with high dielectric constant, while patch antennas require a low loss, low dielectric constant material. The bandwidth and efficiency of the microstrip patch antenna may also increased by selecting a material with a lower dielectric constant.

However, dielectric properties of a polymeric material are not the only consideration in designing a substrate for an electronic device. Processing considerations are also important, such as dimensional stability, resistance to temperature, humidity and aging, resistance to chemicals, tensile and structural strengths, flexibility, machinability, impact resistance, strain relief, conformability, bondability and amenability to cladding.

The dielectric properties of the substrate material, particularly low loss tangent, are important in a microstrip antenna. The structure of the microstrip antenna, including its radiator and transmission line feed, is a well known (see, for example, Bahl et al., Microstrip Antennas, Artech House, 1980; Pozar and Shaubert, eds., Microstrip Antennas-The Analysis and Design of Microstrip Antennas and Arrays, IEEE Press 1995.). In its simplest form, the microstrip patch antenna (MPA) may be a shaped metal conductor fed at one of its edges by an integral microstrip transmission line. This shaped transmission line/radiator structure is typically supported a short distance above a ground plane by a dielectric sheet or layer having a thickness substantially less than one-fourth wavelength at the intended operating frequency of the antenna (generally on the order of one-tenth wavelength or less). The resonance dimension of the shaped radiator patch is typically selected to be one-half wavelength, thus providing a pair of radiating slots between opposed edges (e.g. transverse to the feedline) and the underlying ground plane. The transverse or non-radiant dimension is typically selected, in part, as a function of the desired radiated power. If the non-resonant dimension is on the order of one wavelength or more, multiple feed points may be

provided by, for example, a corporate feed structure network. Microstrip patch antennas are described in numerous patents and publications, such as, for example, U.S. Patent No. 4,887,089 to Shibata, et al., U.S. Patent No. 5,055,854 to Gustafsson, U.S. Patent No. 4,963,891 to Aoyagi et al., U.S. Patent No. 5,070,340 to Diaz, and Tarot, et al., New Technology to Realize Printed Radiating Elements, Microwave and Optical Technology Letters, vol. 9, no. 1, May 1995.

In addition to the MPA, other types of microstrip antennas include microstrip traveling wave antennas, which consist of chain-shaped periodic conductors on a substrate backed by a ground plane. Microstrip slot antennas comprise a slot cut in the ground plane perpendicular to the strip conductor of a microstrip feed line.

Desired antenna characteristics may be obtained with a single microstrip element as described above, but characteristics such as high gain, beam scanning, or steering capability may be obtained by combining discrete radiators into arrays. Microstrip antenna arrays are described in many references, including, for example, U.S. Patent No. 4,173,019 to Williams, and U.S. Patent Nos. 4,914,445 and 4,937,585 to Shoemaker, and references cited therein.

A wide variety of materials are available for use as dielectrics for microstrip antennas (See, for example, Bahl, et al., Microstrip Antennas, pages 317-327 and references cited therein; Carver and Mink, Microstrip Antenna Technology, IEEE Trans. Antennas Propaga, vol. AP-29, no. 1, page 2-24, Jan. 1981.). Typical substrate materials may include polytetrafluoroethylene (PTFE), crystalline thermoplastics such as polystyrene, polyethylene and polypropylene, silicones, polyphenylene oxide (PPO), polyester, polyimides, mica, fiberglass, alumina and beryllia.

Following selection of a dielectric material for a particular application, conventional microstrip antenna structures may be conveniently formed by photochemical etching processes similar to those used in the manufacture of printed circuit boards. A microstrip antenna assembly is formed from a laminate, which in its simplest form is a dielectric sheet material with a thin layer of

conductive metal, such as copper, adhered to its opposed sides. One conductive layer of the laminate normally forms the ground plane, and conductive material may be removed from the opposed layer by chemical etching or similar processes to form the very thin microstrip radiator and interconnected transmission line structure as shaped conductive patches on the dielectric sheet. Examples of laminates for microstrip antennas are described in U.S. Patent No. 4,914,445 to Shoemaker, U.S. Patent No. 4,937,585 to Shoemaker and U.S. Patent No. 4,833,005 to Klaar et al.

As reported in U.S. Patent No. 4,816,836 to Lalezari, an effective microstrip antenna laminate structure should be conformable and mountable to a curved surface. A microstrip antenna is often mounted on an external, curved surface of airplanes, missiles, artillery shells and the like, and mounting to a curved surface provides a low profile and reduces turbulence. Generally, the mounting surface has a convex shape, and the antenna assembly is simply deformed and adhered directly on the curved surface. As the antenna is bent around a small radius curve, the outer convex surface is placed under substantial tension and must stretch, which causes a non-flexible material to crack. The crack ultimately results in deformation and tearing of the copper antenna elements, which pulls the antenna apart. This cracking is a particular problem with rigid, crystalline polymeric materials and foams.

The Lalezari reference describes an antenna with a multi-layer PTFE and fiberglass substrate and a method for mounting the antenna on a curved surface. The antenna structure described in this patent comprises a relatively thin dielectric substrate with antenna elements on a surface thereof, and a second relatively thick dielectric substrate. As shown in Fig. 2 of the Lalezari patent, to adhere the antenna structure to the curved surface, the thick dielectric substrate material 41b must initially be adhered to the curved surface as a spacer. The thinner first dielectric substrate 41a is then adhered to the spacer 41b. The method described in Lalezari illustrates that PTFE dielectric substrates lack the conformability required in many applications. In addition, the multi-layer structure is expensive and difficult to manufacture.

Another desirable characteristic of an antenna dielectric material is weatherability. As noted above, microstrip antennas are typically mounted on external surfaces which are exposed to severe weather conditions, and antenna properties may be significantly affected if the dielectric layer absorbs moisture or has poor thermal stability over its operating temperature range. Liquid water has a very high dielectric constant, and moisture absorption by foamed dielectric substrate materials may significantly detune the antenna and ultimately result in substrate deformation. Conventional foam materials readily absorb moisture and have extremely poor impact resistance, which limits their desirability as antenna substrates or laminate layers.

If weatherability and toughness are a concern, it is well known in the art to select PTFE as a dielectric substrate material for antenna applications. The PTFE may also be reinforced with ceramics or glass fibers, or formed into a cloth laminate. As noted above, these materials are not sufficiently conformable for some applications. PTFE is also difficult to extrude, and is not compatible with many conventional adhesives and antenna materials. In addition, a significant disadvantage is PTFE's high manufacturing cost.

There is a need for a tunable dielectric substrate material which may be manufactured inexpensively and easily in a wide variety of laminate configurations without sacrifice of critical performance properties. At present no low-cost dielectric substrate material is commercially available which provides the desired combination of properties for electronic device design, such as variable ε_r and tan δ, weatherability and toughness, conformability, and processability.

SUMMARY OF THE INVENTION

The present invention is a flexible polymeric substrate material for the mounting of electronic devices which has tunable dielectric properties. In one embodiment, the present invention is low dielectric loss thermoplastic elastomer substrate or laminate material having a loss tangent less than about 0.005. The low loss thermoplastic elastomer of the invention comprises a thermoplastic polymeric component comprising polar or non-polar monomeric units, or mixtures

supplied in the form of a laminate with dielectric properties suited for a particular application.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plot of dielectric constant (ε_r) and loss tangent (tan δ) vs. percent loading for the samples of Examples 7 and 11;

Fig. 2 is a plot of dielectric constant (ε_r) and loss tangent (tan δ) vs. percent loading for the samples of Examples 12-14;

Fig. 3 is a plot of dielectric constant (ε_r) and loss tangent (tan δ) vs. percent loading for the samples of Examples 15 and 17;

Fig. 4 is a plot of dielectric constant (ε_r) and loss tangent (tan δ) vs. percent loading for the samples of Example 33, with the tan δ expressed in milliunits (mu);

Fig. 5 is a plot of dielectric constant (ε_r) vs. time for the samples of Example 35;

Fig. 6 is a plot of loss tangent (tan δ) vs. time for the samples of Example 35; and

Fig. 7 is a plot of the percent change dielectric constant (ε_r) vs. exposure time for the samples of Example 36.

DETAILED DESCRIPTION OF THE INVENTION

The substrate material of the present invention is a polymeric material comprising a thermoplastic elastomer. "Thermoplastic elastomer", as used herein, refers to a class of polymeric substances which combine the processability (when molten) of thermoplastic materials with the functional performance and properties of conventional thermosetting rubbers (when in their non-molten state).

The low loss thermoplastic elastomers of the invention may comprise any thermoplastic polymeric component and any elastomeric polymeric component which provides a predetermined dielectric constant and resultant loss tangent (tan δ) of less than about 0.005, preferably less than about 0.003. The low loss thermoplastic elastomer of the invention comprises a thermoplastic polymeric component comprising polar or non-polar monomeric units, or mixtures thereof, and an elastomeric polymeric component comprising polar or non-polar monomeric units, and specifically excluding mixtures thereof, such that the

thereof, and an elastomeric polymeric component comprising polar or non-polar monomeric units, and specifically excluding mixtures thereof, such that the resultant loss tangent of the thermoplastic elastomer is less than about 0.003. The thermoplastic elastomers may be block copolymers, graft copolymers, or multi-phase dispersions, and multi-phase dispersions having an olefinic thermoplastic component and an elastomeric component of an ethylene-propylene rubber are preferred. A thermoplastic elastomer with a thermoplastic component comprising crystalline polypropylene and an elastomeric component comprising ethylene-propylene-diene monomer (EPDM) are particularly preferred. The dielectric materials of the first embodiment are particularly preferred for use in electronic devices such as microstrip antennas.

In another embodiment, the dielectric material of the present invention is a high dielectric loss thermoplastic elastomer substrate or laminate material having a loss tangent greater than about 0.005 and up to about 0.200. The thermoplastic elastomer of this embodiment of the invention comprises a thermoplastic polymeric component comprising polar or non-polar monomeric units, or mixtures thereof, and an elastomeric polymeric component comprising polar or non-polar monomeric units, or mixtures thereof, such that the resultant loss tangent of the thermoplastic elastomer is greater than about 0.005 and up to about 0.200. The dielectric materials of this embodiment are particularly preferred for use as microwave or radar absorbing materials.

The thermoplastic elastomer substrate material of the invention is compatible with a wide variety of fillers. A sufficient amount of a filler may be added to the thermoplastic elastomer substrate material to provide a predetermined dielectric constant over a broad range of about 1 to about 50, preferably about 2 to about 35. Particularly good low-loss dielectric performance has been observed when the filler material is a doped or undoped "capacitor grade" ceramic, such as barium titanate or lead oxide.

The filled or unfilled substrate material of the invention may be bonded to a wide variety of other dielectric materials and metallic materials, and may be

resultant loss tangent of the thermoplastic elastomer is less than about 0.005, preferably less than about 0.003.

As explained in the Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., vol. 9 at 15, thermoplastic elastomers are typically divided into two principal classes: (a) block or graft copolymers; and (b) multi-phase dispersions.

In the block or graft thermoplastic elastomers, the hard and elastomeric phases are chemically bonded by block or graft polymerization, and have the structure A-B-A or $(A\text{-}B)_n$, where A is a hard or thermoplastic phase and B is a soft or elastomeric phase. For the purpose of the present invention, A-B-A structures are preferred for their superior physical properties. In block/graft thermoplastic elastomers the hard polymer end segments form separate physical regions, referred to as domains, dispersed in a continuous elastomer phase. Most of the polymer molecules have hard segments which act as physical crosslinks at room temperature and tie the elastomer chains together in a three dimensional network. When the material is heated or dissolved in solvents, the domains lose their strength, and the polymer may flow. Upon cooling or solvent evaporation, the domains harden and the three dimensional network retains its physical integrity.

In the low loss embodiment of the present invention, thermoplastic polymeric component A may comprise any polar or non-polar monomeric unit, or mixtures thereof, and elastomeric polymeric component B may comprise any polar or non-polar monomeric unit, specifically excluding mixtures thereof, such that the bonded structure thereof has a resultant loss tangent of less than about 0.005, preferably less than about 0.003.

As noted in the above discussion, polymers with low dielectric loss typically have non-polar or substantially non-polar substituents, and thermoplastic elastomers with thermoplastic and elastomeric polymeric components comprised of non-polar monomeric units are preferred for use in the present invention. The term "non-polar" as used herein refers to monomeric units that are free from dipoles or in which the dipoles are substantially vectorially balanced. In these

polymeric materials the dielectric properties are principally a result of electronic polarization effects,

To provide a low-loss dielectric material in the present invention the thermoplastic polymeric component A may be comprised of the following polar or non-polar monomeric units, for example: styrene, α-methylstyrene, olefins, halogenated olefins, sulfones, urethanes, esters, amides, carbonates, and imides, acrylonitrile, and co-polymers and mixtures thereof. Non-polar monomeric units such as, for example, styrene and α-methylstyrene, and olefins such as propylene and ethylene, and copolymers and mixtures thereof, are preferred. The thermoplastic polymeric component is preferably selected from polystyrene, poly(α-methylstyrene), and polyolefins. Polyolefins are preferred, and polypropylene and polyethylene, and copolymers of propylene and ethylene, are particularly preferred.

The elastomeric polymeric component B in the low-loss dielectric material of the invention may comprise any of the following polar monomeric units, for example: esters, ethers, and copolymers and mixtures thereof. The elastomeric component B may comprise any of the following non-polar monomeric units, for example: butadiene, isoprene, olefins such as ethylene-co-butylene, siloxanes, and isobutylene, and mixtures and copolymers thereof. Mixtures and copolymers of polar and non-polar monomeric units are not contemplated in the elastomeric component of the low-loss thermoplastic elastomers of the invention. Non-polar monomeric units such as butadiene, isoprene olefins, siloxanes and mixtures and copolymers thereof are preferred, and the elastomeric component B is preferably selected from polybutadiene, polyisoprene, poly(ethylene-co-butylene), poly(ethylene-co-propylene), polydimethylsiloxane, polyisobutylene, poly(ethylene-co-butylene), and poly(ethylene-co-propylene).

For example, styrenic block copolymeric thermoplastic elastomers which may be useful in the present invention include linear and/or branched materials having a polybutadiene or polyisoprene elastomeric segment available from Union Carbide Chemicals and Plastics, Danbury, CT, under the trade designations Kraton D and Cariflex, and from Philips Petroleum, Bartlesville, OK under the trade

designation Solprene. Linear styreneic block thermoplastic elastomers having a poly(ethylene-co-butylene) (EB) and a poly(ethylene-co-propylene) (EP) elastomeric segment which may be useful in the present invention include EB/EP materials available from Union Carbide under the trade designation Kraton G, EB materials available from Union Carbide under the trade designation Elexar, polybutadiene or EB materials available from Great Lakes Terminal and Transport Corp. under the trade designation Dynaflex, EB materials available under the trade designation Tekron from Teknor Apex, and EB materials with silicone oils available under the trade designation C-Flex from Concept. Other useful copolymerized thermoplastic elastomers include materials available under the trade designation Engage from Dow, Midland, MI, and Exact from Exxon, Houston, TX.

The block/graft copolymer thermoplastic elastomers which may be used in the present invention may be synthesized by any sequential polymerization and step growth process as well known in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, 4th ed., vol. 9 at 21-25; Handbook of Polyolefins, Vasilie, Seymour, eds. Decker, NY, 1993, pages 943-966.

In the second general class of thermoplastic elastomers, multi-phase materials, at least one phase comprises a material that is hard at room temperature, but becomes fluid upon heating, and another phase comprises a softer material that is rubber-like at room temperature. The multi-phase thermoplastic elastomers typically consist of a thermoplastic polymeric component and more rubber-like elastomeric polymeric component. The two components normally form finely dispersed single phase or multiphase systems. The rubber-like phase may be crosslinked during high shear mixing as part of a well known procedure referred to as "dynamic vulcanization". See, for example, U.S. Patent No. 3,037,954 to Gessler.

In the low loss multi-phase structures of the present invention, the thermoplastic polymeric component preferably comprises any polar or non-polar monomeric unit normally regarded as a thermoplastic, and mixtures and co-polymers thereof. The elastomeric component preferably comprises any polar or

non-polar monomeric unit normally regarded as elastomeric, specifically excluding mixtures thereof, such that the multi-phase dispersion has a resultant loss tangent of less than about 0.005, preferably less than about 0.003.

The thermoplastic component of the low-loss multi-phase thermoplastic elastomers of the invention may be comprised of the following polar and non-polar monomeric units: olefins, such as propylene and ethylene, vinyls and mixtures and co-polymers thereof. For the purpose of the present invention, the thermoplastic polymeric component is preferably selected from non-polar monomeric units, and polyolefins, particularly polypropylene and polyethylene, and copolymers with ethylene and propylene monomeric units, are preferred. Isotactic polypropylene is particularly preferred for use as the thermoplastic polymeric component.

The elastomeric polymeric component of the low-loss multi-phase thermoplastic elastomers of the invention may be comprised of crosslinked or uncrosslinked polar rubbers such as nitrile rubber, or crosslinked or uncrosslinked non-polar rubbers such as butyl rubber, natural rubber, ethylene-propylene rubber (EPR), ethylene-propylene diene rubber (EPDM) and silicone rubber. Crosslinked or uncrosslinked non-polar rubbers are preferred, and EPR and EPDM are particularly preferred. The elastomeric rubber component may be uncrosslinked (green), or may be partially or fully crosslinked using typical crosslinking agents (e.g. phenolics and peroxides) during mixing or as part of the dynamic vulcanization process.

Examples of multi-phase thermoplastic elastomers having a crystalline polypropylene thermoplastic polymeric component and EPR or EPDM elastomeric polymeric component which are preferred for use in the low-loss dielectric materials of the present invention include blends available under the trade designations TPR from Advanced Elastomer Systems, Ren-Flex from Dexter, Polytrope from Schulman, Telcar from Teknor Apex, Ferroflex from Ferro, WRD or SRD Series from Union Carbide, and HiFax from Montell USA, Wilmington, DE, and the like. Dynamically vulcanized blends with a crystalline polypropylene thermoplastic polymeric component and an EPDM elastomeric polymeric component which may be used in the present invention include materials

available under the trade designations Santoprene from Advanced Elastomer Systems, Sarlink 3000 from Novacor, Telprene from Teknor Apex and HiFax XL from Montell USA. Dynamically vulcanized blends having a polypropylene thermoplastic component and a butyl rubber elastomeric component are available under the trade designations Trefsin from Advanced Elastomer Systems and Sarlink 2000 from Novacor. Dynamically vulcanized blends having a polypropylene thermoplastic component and a natural rubber elastomeric component which may be useful in the present invention are available under the trade designation Vyram from Advanced Elastomer Systems.

The multi-phase thermoplastic elastomers which may be used in the present invention may be compounded using a wide variety of conventional procedures. The thermoplastic elastomers are typically produced by mechanically mixing the hard thermoplastic polymeric component and the rubber-like elastomeric polymeric component under high shear or by extrusion, although it is sometimes possible to produce the thermoplastic elastomer in situ in a reactor during polymerization. See, for example, Legge, Holden and Schroeder, eds., Thermoplastic Elastomers-A Comprehensive Review, Oxford University Press, 1987; Handbook of Polyolefins, Vasilie, Seymour, eds. Decker, NY, 1993, pages 943-966.

Of the above described thermoplastic elastomers, the multi-phase combinations are preferred for use in the low-loss dielectric materials of the present invention. Of the thermoplastic olefinic polymeric components, propylene and ethylene are preferred, and crystalline, isotactic polypropylene is particularly preferred. Crosslinked or uncrosslinked EPDM is particularly preferred as the elastomeric polymeric component in the present invention, and uncrosslinked EPDM is most preferred for its combination of physical properties and low cost. Materials which may be used in the present invention are described in U.S. Patent Nos. 3,876,454 and 3,470,127 to Snell et al. The relative proportions of polypropylene thermoplastic component and the EPDM elastomeric component will vary widely depending on the combination of properties desired in a particular application.

Multi-phase thermoplastic elastomers which are particularly preferred for use in the present invention are available under the trade designations HiFax from Montell USA of Wilmington, DE, and WRD/SRD and the like from Union Carbide, Danbury, CT. The HiFax materials are blends of crosslinked or non-crosslinked rubber, such as EPDM, EPR or butyl, with an isotactic olefin plastic such as polyethylene or polypropylene. A particularly preferred material, for reasons of cost and processability, referred to by the manufacturer as a "thermoplastic olefin", is HiFax CA10, a blend of a noncrosslinked (green) rubber, preferably EPR or EPDM, most preferably EPDM, with crystalline polypropylene. As reported by the manufacturer, the HiFax CA10 includes greater than about 60% by weight of the polypropylene thermoplastic component and about 40% by weight of the EPR/EPDM elastomeric component., a Shore Hardness of about 40D as measured according to ASTM D-2240, and tensile strength of about 2200 Psi as measured according to ASTM D-636. The non-crosslinked rubber component is reported to function as a non-migratory polymeric plasticizer, and the HiFax CA10 material has good flex fatigue resistance.

The neat thermoplastic elastomers used in the low-loss materials of the present invention should have a dielectric constant of less than about 3, preferably less than about 2.5, and the loss tangent (tan δ) should preferably be less than about 0.003. Since polarization is substantially instantaneous in these materials, the dielectric constant and loss tangent will be substantially independent of frequency, and such independence is expected over a wide frequency range, at least from about 300 MHz to about 20 GHz. A wide variety of measurement apparatus may be used to determine the dielectric properties of a polymeric material, but for the purposes of the present invention an RF impedance/material analyzer, such as the 4291A available from Hewlett Packard, is preferred.

In another embodiment, the dielectric material of the present invention is a high dielectric loss thermoplastic elastomer substrate having a loss tangent of greater than about 0.005 up to about 0.200. The thermoplastic elastomer of the invention comprises a thermoplastic polymeric component comprising polar or non-polar monomeric units, or mixtures thereof, and an elastomeric polymeric

component comprising polar or non-polar monomeric units, or mixtures thereof, such that the resultant loss tangent of the thermoplastic elastomer is greater than about 0.005 and up to about 0.200. To provide a dielectric material with high dielectric loss, a thermoplastic polymeric component comprising polar monomeric units and an elastomeric thermoplastic component comprising polar monomeric units are preferred.

However, the dielectric constant and loss tangent of a thermoplastic elastomeric material may be tailored for a specific application by adding a sufficient amount of a filler to provide a predetermined dielectric constant of from about 1 to about 50, preferably about 2 to about 35, while maintaining the loss tangent at a predetermined level as described above. For example, fillers which may be added to the thermoplastic elastomers to tune their dielectric properties for a particular application include well known materials such as silica, alumina, glass bubbles, barium titanate ($BaTiO_3$), lead oxide (PbO) titanium dioxide (TiO_2) and mixtures thereof. Preferred for use as fillers in the present invention are titanates with a perovskite crystalline structure, often referred to in the art as "capacitor grade" ceramics. These titanates may be doped with a wide range of impurities, such as, for example, niobium, to tailor their dielectric properties for a particular application. Particularly preferred for use in the present invention are solid state reacted powders, available in a non-crystalline or a sintered form under the trade designation TICON from TAM Ceramics, Niagara Falls, NY. Particularly preferred capacitor grade ceramics include materials available under the trade designations TICON COF 40, TICON COF 50, TICON COF-70, TICON CN and TAMTRON Y5V183U and Y5V153G from TAM Ceramics.

The fillers used in the present invention may also include other polymeric materials. For example, to tailor dielectric and/or physical properties for a particular application, a polymer may be mechanically blended with the filled or unfilled thermoplastic elastomer of the invention to create a dispersion of the polymer in the thermoplastic elastomer. The use of polymeric fillers allows even greater flexibility in controlling the dielectric and/or mechanical properties of the thermoplastic elastomers of the invention.

The amount of filler added will depend on the dielectric constant and loss tangent required for a particular application, but a range of up to about 70% by volume of thermoplastic elastomer, preferably about 5% to about 60% by volume, is preferred. If the filler loading is greater than about 60-70% by volume, the physical properties of the resultant material, particularly its flexibility and tensile strength, may be adversely affected. The fillers may be compounded with the thermoplastic elastomers using any conventional method such as calendering, extrusion, and dry blending, or combinations thereof.

The dielectric properties of the loaded or unloaded thermoplastic elastomers should remain relatively constant when the material is exposed to moisture as evaluated water absorption according to test procedures generally outlined in ASTM C272. The dielectric properties of the loaded or unloaded thermoplastic elastomers should remain relatively constant over a wide range of temperatures of about -50 °C to about 100 °C, preferably about -30 °C to about 70 °C.

The thermoplastic elastomer selected for use in the present invention should be flexible when bent around a mandrel and conformable to a convex surface, preferably without fracture or stress whitening. Preferably, the thermoplastic elastomer should not break or stress whiten when bent around a mandrel of diameter less than about 1 inch (2.5 cm), more preferably when bent around a mandrel with diameter less than about 0.5 inch (1.25 cm), and most preferably when bent around a mandrel of diameter of about 0.125 inch (0.318 cm) according to a test procedure generally outlined in ASTM D522. The dielectric properties of the loaded or unloaded thermoplastic elastomer should also remain stable when the material is bent around a mandrel or conformed to a convex surface.

The loaded or unloaded thermoplastic elastomers which are used in the present invention may be easily processed into sheet films using an extruder, and may optionally be uniaxially or biaxially oriented. The sheet films may have a wide range of thicknesses and their dielectric properties may be tailored for a specific application. The thermoplastic elastomers of the invention may be readily

bent around rolls during web processing, which makes possible prime coating, adhesive coating or converting operations on the dielectric material.

As is well known in the art, glass fibers, glass or alumina cloth, silica, quartz, ceramic powder and the like may be added to enhance the physical properties of the thermoplastic elastomer. The amount of filler added to the thermoplastic elastomer to enhance physical properties will also depend on the application, but, as is well known in the art, high loadings of filler may alter the flexibility and/or ultimate tensile strength of the thermoplastic elastomer material.

The thermoplastic elastomer used in the present invention may be treated with corona discharge or other surface treatments to enhance its physical properties. The porosity of the loaded or unloaded thermoplastic elastomer may be controlled to tailor dielectric properties. Methods of enhancing porosity include adding a chemical foaming agent, injecting an inert gas such as nitrogen or fluorocarbon, or by compounding with a plasticizer and subsequent extraction of the plasticizer as described in U.S. Patent No. 4,963,891 to Aoyagi et al. Again, while increasing porosity may enhance dielectric properties, porosity may adversely affect the physical properties of the material.

The thermoplastic elastomers of the present invention may be provided in the form of laminates. The laminates of the invention may be one-ply, which considerably simplifies the manufacturing process compared to conventional substrate materials for electronic applications. Single or multiple layers of the thermoplastic elastomer substrate, or a layer of thermoplastic elastomer and one or more layers of another dielectric material, may laminated on one side or on both sides with one or more layers of a metal, such as, for example, gold, silver, copper, aluminum, electrolytic or low oxygen content copper, nickel, chromium, alloys available under the trade designation Inconel, and alloys thereof. The metallic layer may be coated with an anticorrosive coating. An optional adhesion promoter may be added between the metallic layer and the thermoplastic elastomer substrate. A conductive ink, spray or epoxy may serve as the metallic layer as described in U.S. Patent No. 4,937,585 to Shoemaker.

The thickness of the thermoplastic elastomer substrate layer may vary widely depending on the intended application.

The substrate may be further laminated to additional dielectric layers and/or metallic layers to provide a laminate structure with specific dielectric and physical properties. The additional dielectric layers may be polar or non-polar, can exhibit differing crosslinking densities and/or dielectric properties, or can contain differing reinforcing or dielectric enhancing materials such as those mentioned above. For example, the additional dielectric layer(s) may comprise polyolefins, polyamides, polyethylene terepthalate, and polar or non-polar thermoplastic elastomer which may be the same or different from the thermoplastic elastomer in the substrate.

The thermoplastic elastomer/metallic layer laminate may be further laminated to an additional reinforcing layer of a polymeric material, or may be laminated on two sides with a polymeric material, which may be the same or different. The thermoplastic elastomer/metallic laminate of the invention may be further laminated to other reinforcing materials, such as, for example, to a circuit board material such as FR-4 or the like, or to a metallic sheet. The metallic layer may be covered with an optional removable protective sheet if desired. In addition, copper damage inhibitors, anti-ultraviolet agents, antioxidants and the like may be added to any of the laminate layers.

Of course, the metallic layer or layers on the laminate of the invention may be processed in any manner known in the art, such as by chemical etching, laser ablation, masking processes and the like, to produce any electronic circuit structure. Some examples are described in co-pending U.S. application No. 08/609,092, and include a microstrip antenna radiating patch with or without a feed line, a ground plane structure, or a network of radiating patches to provide an antenna array.

The bonding of the metallic layer to the thermoplastic elastomer substrate of the invention may be performed by any method known in the art. For example, a pressure sensitive adhesive (PSA) may be applied to the thermoplastic elastomer substrate using any conventional lamination system, and the metallic layer may be

applied to the PSA with conventional lamination techniques. In the alternative, the metallic layer may be hot laminated to the thermoplastic elastomer substrate using a heated press, available from Carver or Rucker. For example, the laminates may be prepared at a temperature of about 350 °F (175 °C) under a pressure of about 10,000 psi (70 MPa) to about 60,000 psi (400 MPa). A curing time of less than about 10 minutes is preferred. The metallic layer may also be applied to the thermoplastic elastomer substrate using sputtering, stamping or vacuum deposition techniques as is well known in the art. The laminates may be prepared as a continuous web or by processing laminate sheets using a hot lamination procedure.

EXAMPLES

The following non-limiting examples will illustrate the present invention. All percentages by weight will be based upon the total weight of resin plus filler, unless otherwise specified.

Example 1

The samples in Example 1 were prepared from an unfilled (i.e., lacking a high ε_r filler) dielectric resin comprised of a UV stabilized, non-crosslinked rubber modified polypropylene blend. The resin (natural, without colorant) is commercially available from Montell USA, Wilmington , DE, under the trade designation HiFax CA10G. The melt flow rate of this material has been listed in Montell's product literature as 0.5 to 0.7 g/10 minutes as measured by ASTM D1328, and its density is reported as 0.87 g/cc.

The resin was extruded using a Haake Rheocord single screw extruder to yield films with thicknesses varying from about 5 mils (0.013 cm)to about 60 mils (0.152 cm). The diameter of the single screw was 3/4 inch (1.91 cm). The processing conditions during extrusion included a die temperature of 440 °F (227°C) and extruder temperatures of 325 °F (163 °C) in zone 1, 420 °F (216 °C) in zone 2, and 440 °F (227 °C) in zone 3.

The die extrudate (die width: 5 inches (13 cm)) was cast onto a 2 mil (0.005 cm) polyester film carrier which passed over a chrome chill roll and under a silicone back-up roll. The chill roll was set at a temperature of 50 °F (10 °C).

The dielectric properties of the films were tested at 905 MHz at room temperature (23 °C) using an RF impedance/material analyzer commercially available from Hewlett Packard, under the trade designation HP 4291A. The test utilized a capacitance measurement modified for high frequency. A dielectric test fixture commercially available from Hewlett Packard, under the trade designation HP 16453A was used in conjunction with the material analyzer.

The dielectric properties of the films are shown in Table 1 below. The maximum error in the values of ε_r as reported by Hewlett Packard for the HP 4291A material analyzer are about ± 5%. Measured tan δ values ≤ 0 have been reported as < 0.002 in all tables, and as 0.002 in all plots.

TABLE 1

Example	Description	905 MHz	
		ε_r	Tan δ
1	HiFax CA 10G	2.25	0.0002
2	HiFax XL 42D01	2.35	0.0014
3	HiFax XL 42D01-Black	2.41	0.00026
4	HiFax XL 65 A01	2.28	< 0.002
5	HiFax XL 75 A01	2.28	0.00024
6	HiFax XL 85A01	2.29	0.0015
19	Union Carbide WRD-7-507	2.06	< 0.002

Example 2

The samples of Example 2 were prepared from an unfilled dielectric film comprised of a partially crosslinked, rubber modified polypropylene. The resin (natural, without colorant and without UV stabilization) is commercially available from Montell USA under the trade designation HiFax XL 42D01. The resin was extruded using a Haake Rheocord single screw extruder to yield a film with a thickness of 33 mils (0.084 cm). The diameter of the single screw was 3/4 inch (1.91 cm) and a die with a 5 inch (12.7 cm) width was used. The processing conditions during extrusion included a die temperature of 320 °F (160 °C) and extruder temperatures of 290 °F (143 °C) in zone 1, 310 °F 154 °C) in zone 2, and 320 °F (160 °C) in zone 3. The die extrudate was cast onto a 2 mil (0.005 cm) polyester film carrier which passed over a chrome chill roll and under a silicone back-up roll. The temperature of the chill roll was set at 50 °F (10 °C).

The dielectric properties of the films of Example 2 were measured by the RF impedance/material analyzer at 905 MHz as described in Example 1. The results are shown in Table 1.

The film of Example 2 was also tested by a 7 mm coax waveguide technique for broadband frequency measurements conducted from approximately 500 MHz to 20 GHz. The film of Example 2 displayed a flat response of ε_r over this broad frequency range.

Example 3

The samples of Example 3 were prepared from a carbon black filled dielectric film comprised of a partially crosslinked rubber modified polypropylene resin. The resin (black, but without extra UV stabilization) is commercially available from Montell USA under the trade designation HiFax 42D01-Black.

The resin was extruded using a 1.5 inch (3.8 cm) single screw extruder to yield a 14 inch (35.6 cm) wide film with an approximate thickness of 45 mils (0.114 cm). The processing conditions during extrusion included a die temperature of 350 °F (177 °C) and extruder temperatures of 300 °F (149 °C) in zone 1, 320 °F (160 °C) in zone 2, 340 °F (171 °C) in zone 3, and 370 °F (188°C) in zone 4. The extrudate was cast onto a chrome chill roll and passed under a silicone back-up roll. The chill roll was set at a temperature of approximately 50°F (10 °C).

Dielectric properties of the films were measured by the RF impedance/material analyzer at 905 MHz as in Example 1, and results are shown in Table 1.

Examples 4-6

The samples of Examples 4-6 were prepared from unfilled dielectric films in the form of injection molded plaques comprised of partially crosslinked rubber modified polyolefin resin. The resin was natural, without colorants or UV stabilization. The plaques are commercially available from Montell USA under the trade designations HiFax XL 65A01 (Example 4), HiFax XL 75A01 (Example 5), and HiFax XL 85A01 (Example 6).

The films were tested by the RF impedance/material analyzer at 905 MHz as described in Example 1, and the results are shown in Table 1.

Example 7

The samples of Example 7 were prepared by adding solid state, niobium-doped, barium titanate ceramic to a polymer melt of HiFax CA10G resin used in Example 1. The ceramic is commercially available from Tam Ceramics, Inc.,

Niagara Falls, NY, under the trade designation Ticon COF 70. Ticon COF 70 is described in the Tam Ceramics' product literature as being comprised of > 97 % by weight barium titanate and having major impurities of SrO (0.7%), Nb_2O_5 (0.25 %) and SO_3 (0.2%) with other more minor impurities also being listed. A typical particle size distribution for Ticon COF 70 is listed at D50 = 1 micron, and its density is listed as 5.8 g/cc.

The Ticon COF 70 ceramic material was added to the polymer melt at 210 °C by a Haake Rheocord System 40 microprocessor controlled torque rheometer used in conjunction with a Haake Rheomix Mixer (model 600). A charge of 43 % by weight (10% by volume) of Ticon COF 70 was added to the polymer (48 cc total volume) and mixed, to form a composite, by two rotating blades at 40 rpm for 30 minutes to ensure complete mixing. After mixing, the composite was placed between two pieces of polyester liner which were then placed between two 12" X 12" (30 cm X 30 cm) stainless steel platens. The platens containing the composite in cooled, globular form were inserted into a heated Carver Laboratory Press (25 ton hydraulic press, model 2518) and the platens were then heated to a temperature of 210 °C. A maximum hydraulic pressure of 30,000 lbs (14,000 kg) was applied which pressed the sample into a film of approximately 7 inch (18 cm) diameter and a thickness of approximately 40-60 mils (0.10-0.15 cm)suitable for testing of dielectric properties. Film thickness was controlled by shims which were inserted between top and bottom release liners.

The dielectric properties of the films of Example 7 were tested by the RF impedance/material analyzer of Example 1 at 905 MHz, and the results are shown in Fig. 1.

Examples 8-10

The samples of Examples 8-10 were prepared by adding Ticon COF 70 described in Example 7 to a HiFax CA10G resin described in Example 1. The Ticon COF 70 and the HiFax CA10G were compounded to form a composite with the following weight percentages of Ticon COF 70: 10% by weight (1.64 % by volume) (Example 8), 30% by weight (6.04 % by volume) (Example 9), and 50%

by weight (13 % by volume) (Example 10), on a 33 mm APV MP2030TC co-rotating twin screw compounder with an attached 2 inch (5 cm) pelletizer available from Berlyn under the trade designat·ɔn PELL2, which included a 2 hole pelletizing die and a water cooling trough. Each composite was added to a gravimetric feeder which fed the composite to the twin screw extruder. The extrudate then passed from the pelletizing die (430 °F, 221 °C) into the water trough and lastly, the two strands were chopped to pellets of a suitable size for extrusion. The compounded pellets were then extruded into 20 mil thick films using a Haake Rheocord 3/4 inch (1.91 cm) single screw extruder and a 5 inch (12.7 cm) width die (65 mil (0.165 cm) die shims).

The processing conditions included a die temperature 450°F (232 °C) and; extruder temperatures of 330 °F (166 °C) in zone 1, 425 °F (218 °C) in zone 2, and 450 °F (232 °C) in zone 3. The die extrudate was cast onto a 2 mil polyester film carrier which passed over a chrome chill roll and under a silicone back-up roll. The chrome chill roll was set at a temperature of 52 °F (11 °C).

The dielectric properties of the films of Examples 8-10 were measured by the RF impedance/material analyzer at 905 MHz as described for Example 1, and the results are shown in Table 2 below. The dielectric properties were also measured at 5.6 GHz by a double split post resonator technique, and the results are also shown in Table 2.

TABLE 2

Example	Description	Vol. Loading (%)	εr (905 MHz)	tan δ (905 MHz)	εr (5.6 GHz)	tan δ (5.6 GHz)
8	Ticon COF 70 in HiFax CA10G	1.6	2.41	<0.002	2.39	0.0011
9	Ticon COF 70 in HiFax CA10G	6.0	2.52	<0.002	2.60	0.0021
10	Ticon COF 70 in HiFax CA10G	13.0	2.83	<0.002	2.94	0.0026
16	Tamtron Y5V183U in HiFax CA10G	9.8	2.58	<0.002	2.60	0.0014
17	Tamtron Y5V183U in HiFax CA10G	50	17.5	0.0047	—	—
18	R101 Titanium Dioxide in HiFax CA10G	17.0	2.74	<0.002	2.95	0.0014

Example 11

The samples of Example 11 were prepared by adding the Ticon COF 70 ceramic material described in Example 7 to a HiFax CA10G resin described in Example 1 in the form a polymer melt. The Ticon COF 70 was added to the polymer melt at 87% by weight (50 % by volume) to obtain a high dielectric constant sample. The Ticon COF 70 was added to the polymer melt at a temperature of 410 °F (210 °C) using the mixing system of Example 7. After adding the Ticon COF 70, the resulting melt was mixed at 40 rpm for 30 minutes using. The composite was pressed into a film sample using the technique described in Example 7.

The films were tested by the RF impedance/material analyzer at 905 MHz as in Example 1, and the results are shown Fig. 1.

Example 12

The samples of Example 12 were prepared by adding 50% by weight (13% by volume) of a capacitor grade ceramic composition commercially available from Tam Ceramics under the trade designation Tamtron Y5V153G to the HiFax CA10G resin of Example 1 in the form of a polymer melt at a temperature of 410 °F (210 °C) by the mixing method of Example 7. The Tamtron Y5V153G was described in the Tam Ceramics product literature as being comprised of 85-90 % by weight barium titanate and having major impurities of: barium zirconate (5-10 % by weight) and lesser quantities of calcium stannate (1-5 % by weight), and the density of the material was 5.8 g/cc. The addition of zirconia to the barium titanate ceramic results in a shift to a higher dielectric constant at room temperature. The particle size of this ceramic is 5-10 microns.

The pressing technique as described in Example 7 was used to form a composite and the composite was pressed into a film sample of suitable dimensions for dielectric measurements.

The films of Example 12 were tested by the RF impedance/material analyzer at 905 MHz as described in Example 1, and the results are shown in Fig. 2.

Examples 13-14

The samples of Examples 13-14 were prepared by adding 87% by weight (50% by volume) (Example 13) and 91% by weight (60% by volume) (Example 14) of a capacitor grade ceramic composition commercially available from Tam Ceramics under the trade designation Tamtron Y5V153G to the HiFax CA10G resin of Example 1 in the form of a polymer melt at a temperature of 410 °F (210°C) using the mixing method of Example 7. The pressing technique as described in Example 7 was used to form composites and the composites were pressed into film samples for dielectric measurements.

The films of Examples 13-14 were tested by the RF impedance/material analyzer at 905 MHz as in Example 1, and the results are shown in Fig. 2.

Example 15

The samples of Example 15 were prepared by adding 70% by weight (20% by volume) of a uniform, pre-milled dielectric ceramic commercially available from Tam Ceramics under the trade designation Tamtron Y5V183U to the HiFax CA10G resin (in the form of a polymer melt) described in Example 1 at a temperature of 410 °F (210 °C) by the mixing method of Example 7. The Tamtron Y5V183U was described in the Tam Ceramics product literature as being comprised of 65-75 % by weight lead oxide, 1-5 % by weight magnesium oxide, 1-5 % by weight titanium dioxide and < 0.1 % by weight silicon dioxide, and the density was 8.0 g/cc. Typical particle size is listed at 1.4 microns.

The pressing technique as described in Example 7 was used to form a composite and the composite was pressed into a film sample for dielectric measurements.

The films of Example 15 were tested by the RF impedance/material analyzer at 905 MHz as in Example 1, and the results are shown in Fig. 3.

Example 16

The samples of Example 16 were prepared by adding 50% by weight (10% by volume) of the ceramic of Example 15, Tamtron Y5V183U, to the resin of Example 1, HiFax CA10G. The ceramic and resin were compounded into a composite and pelletized according to the method described in Examples 8-10. The composite, in the form of pellets, was then extruded into 20 mil film using the single screw extruder described in Examples 8-10.

The films of Example 16 were tested by the RF impedance/material analyzer at 905 MHz as in Example 1, and at 5.6 GHz as in Example 8, and the results are shown in Table 2.

Example 17

The samples of Example 17 were prepared by adding 90% by weight (50% by volume) of the ceramic of Example 15, Tamtron Y5V183U, to the resin of Example 1, HiFax CA10G (in the form of a polymer melt) at a temperature of 410 °F (210 °C) by the mixing method of Example 7. The pressing technique as described in Example 7 was used to form a composite and the composite was pressed into a film sample for dielectric measurements.

The films of Example 17 were tested by the RF impedance/material analyzer at 905 MHz as in Example 1, and at 5.6 GHz as in Example 8, and the results are shown in Fig. 3 and Table 2.

Example 18

The samples of Example 18 were prepared by adding 50% by weight (17% by volume) of rutile titanium dioxide, density 4.26 g/cc, commercially available from DuPont de Nemours & Company, Wilmington, DE, under the trade designation R101 to the resin of Example 1, HiFax CA10G. The R101 was compounded with the HiFax CA10G to form a composite and pelletized in the method described in Examples 8-10. The composite, in the form of pellets, was then extruded into 20 mil (0.051 cm) film using the single screw extruder described in Examples 8-10.

The films were tested by the RF impedance/material analyzer at 905 MHz as in Example 1, and at 5.6 GHz as in Example 8, and the results are shown in Table 2.

Example 19

The samples of Example 19 was prepared using a rubber modified thermoplastic elastomer resin commercially available from Union Carbide Chemicals and Plastics, Danbury, CT, under the trade designation WRD-7-507. This resin, comprised of 38% ethylene propylene rubber ("EPR") in polypropylene, was extruded using a Haake Rheocord 3/4" (1.91 cm) single screw extruder to yield a 20 mil (0.051 cm) thick film. The processing conditions included a die temperature of 440 °F (227 °C) and extruder temperatures of 400 °F (204 °C) in zone 1, 420 °F (216 °C) in zone 2, and 440 °F (227 °C) in zone 3. The die extrudate (die width: 5 inches, (13 cm)) was cast onto a 2 mil (0.005 cm) polyester film carrier and passed over a chrome chill roll and under a silicone back-up roll. The water cooled chill roll was set at a temperature of 53 °F (12 °C).

The films were tested by the RF impedance/material analyzer at 905 MHz as in Example 1, and the results are shown in Table 1.

Examples 20-21

The samples of Examples 20-21 utilized laminate structures comprised of sputtered copper on film of either HiFax CA10G (Example 20) or HiFax 42D01 (Example 21). In each sample, 150-200 nm of copper was directly sputtered onto one surface of a 45 mil (0.114 cm) (Example 20) or 28 mil (0.071 cm) (Example 21) thick extruded film to produce a laminate structure with a sputtered copper layer on a polymer layer.

Examples 22-23

The samples of Examples 22-23 utilized laminate structures comprised of copper foil on film of HiFax CA10G (Example 22) or HiFax 42D01 (Example 23).

On each sample 1 mil copper foil containing an acrylic pressure sensitive adhesive (1 mil (0.0025 cm) thick) was prepared by lamination of the adhesive to one surface of the metal foil. The copper foil/PSA was laminated to a 60 mil (0.152 cm) (Example 22) or 28 mil (0.071 cm) (Example 23) thick extruded film to produce a laminate structure with the following layers:
copper foil/PSA/polymer.

Examples 24-25

The samples in Examples 24-25 utilized laminate structures comprised of copper foil on film of either HiFax CA10G (Example 24) or HiFax 42D01 (Example 25). To each film a 1 mil copper foil containing the acrylic pressure sensitive adhesive described in Example 22 was laminated to both sides of a 60 mil (Example 24) or 28 mil (Example 25) thick extruded film to produce a laminate structure with the following layers:
copper foil/PSA/polymer/PSA/copper foil.

Examples 26-27

The samples of Examples 26-27 utilized laminate structures comprised of sputtered copper on a carrier film of polyester adhesively bonded to either one or both sides of either HiFax CA10G (Example 26) or HiFax 42D01 (Example 27). A film of 180 nm sputtered copper on 2 mil (0.0051 cm) polyester film (PET) containing a 5 mil (0.0127 cm) thick acrylic pressure sensitive adhesive was laminated to one or both sides of a 60 mil (0.152 cm) (Example 26) or 28 mil (0.071 cm) (Example 27) thick extruded film to produce laminate structures with the following layers:
PET/copper/PSA/polymer/PSA/copper/PET.

Examples 28-29

The samples of Examples 28-29 utilized laminate structures comprised of aluminum foil on one surface of film of either HiFax CA10G (Example 28) or HiFax 42D01 (Example 29). A sheet of 3 mil aluminum foil (no adhesive) was

directly laminated to one surface of a 60 mil (0.152 cm) (Example 28) or 28 mil (0.071 cm) (Example 29) thick extruded film by a hot lamination technique to produce laminate structures.

Hot lamination of the aluminum layer to the films was completed using a Rucker Press (400 ton) using the following processing conditions: cycle dwell times: preheat 10 sec, emboss 20 sec, and cure 6.0 minutes. The zone temps in the press were: zone 1=350 °F (177 °C), zone 2=350 °F (177 °C), zone 3=350 °F (177 °C), and zone 4= 350 °F (177 °C). The 2 zone pressures were: low pressure =10,000 psi (70 MPa), high pressure = 60,000 psi (400 MPa).

The resulting laminates had the following layered structure: Al foil/polymer.

Examples 30-31

The samples of Examples 30-31 utilized laminate structures comprised of aluminum foil on both surfaces of films HiFax CA10G (Example 30) or HiFax 42D01 (Example 31). A layer of 3 mil (0.0076 cm) thick aluminum foil (no adhesive) was directly laminated to both surfaces of a 60 mil (0.152 cm) (Example 30) or 28 mil (0.071 cm) (Example 31) thick extruded film by the hot lamination technique of Examples 28-29 to provide a laminate structure with the following layers: Al foil/polymer/Al foil.

Example 32

The sample of Example 32 utilized a hot lamination technique to bond the structure comprised of the film of Example 1 bonded to the sputtered side of the laminate of Example 20. The resulting laminate structure was: polymer/sputtered copper/polymer.

Example 33

Other polymers may be blended with the thermoplastic elastomeric polymers of the invention to provide a dispersion with enhanced dielectric properties. For example, when polyvinylidene fluoride available under the trade

designation KYNAR 2750 PVDF from Elf Atochem, Philadelphia, PA, is added to the thermoplastic elastomer HIFAX XL42D01 initially described in Example 2, the ε_r in the resulting mixture increases. As shown in Fig. 4, the polymeric filler increased the ε_r of the blend from 2.30 to 2.37.

Example 34

The films of Examples 1-2 were tested for flexibility by a Mandrel Bend Test generally outlined in ASTM D522. One inch (2.5 cm) strips of the films were placed over test mandrels of varying diameters. Using steady pressure, the test strip was bent approximately 180° around the mandrel at a uniform velocity in a time of less than about 5 sec. The films were removed and examined for cracking or stress whitening visible to the unaided eye. The procedure was repeated using mandrels of successively smaller diameter, the smallest diameter tested being 0.125 inch (0.318 cm). Results of the Mandrel Bend Test are shown in Table 3.

TABLE 3

	Sample Identification									
	CA10G	42D01	FR-4	Rogers 5880	Rogers 4003	Rogers 3003	Rogers 3006	Rogers 3010	Polyguide	Rohm 71
Sample Thickness (inch)	0.058	0.066	0.070	0.127	0.061	0.060	0.050	0.050	0.059	0.120
(cm)	0.147	0.168	0.178	0.323	0.155	0.152	0.127	0.127	0.150	0.305
Mandrel Diameter										
30 inch (76 cm)	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
18 inch (46 cm)	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
12 inch (30.5 cm)	pass	pass	pass1	pass1	pass1	pass	pass	pass	pass	pass
6.5 inch (16.5 cm)	pass	pass	pass1	pass1	pass1	pass	pass	pass	pass	pass
3.38 inch (8.59 cm)	pass	pass	fail2	pass2	fail3	pass	pass	pass	pass	fail3
1 inch (2.5 cm)	pass	pass	fail2	fail3	fail3	pass	pass	pass	pass1	fail3
0.5 inch (1.3 cm)	pass	pass	fail2	fail3	fail3	pass	pass	pass	pass1	fail3
0.38 inch (0.97 cm)	pass	pass	fail2	fail3	fail3	pass4	pass4	pass4	pass1	fail3
0.25 inch (0.64 cm)	pass	pass	fail2	fail3	fail3	pass5	pass5	pass5	pass1	fail3
0.125 inch (0.318 cm)	pass	pass	fail2	fail3	fail3	pass5	pass5	pass5	pass4	fail3

Legend

1. very difficult to bend since rigid
2. could not bend around mandrel since to rigid
3. sample broke
4. stress whitening
5. severe stress whitening

Note: Rogers 3003, 3006, 3010 and 4003 are products or ROGERS CORPORATION
Polyguide is a product of POLYFLON
CA10G (HIFAX XL CA10G) and 42D01 (HIFAX XL 42D01) are products of MONTELL USA

Example 35

The dielectric constant and loss tangent of the films of Examples 1-2 were measured at 905 MHz according to the procedure in Example 1.

The films were tested by the Water Absorption Test according to the procedure outlined in ASTM D272. Tared samples of the films were completely immersed in water at 23 °C for 46 hours at room temperature and subsequently weighed after all surfaces were blotted to remove traces of surface water.

Percent weight gain of water was recorded for 1 inch X 3 inch (2.5 cm X 8 cm) samples, and the dielectric properties were re-measured according to the procedure in Example 1.

Fig. 5 illustrates the dielectric constant (ε_r) data for the Water Absorption Test, while the loss tangent (tan δ) data are shown in Fig. 6.

Example 36

Example 36 utilized unfilled dielectric films comprised of partially crosslinked, rubber modified polypropylene resins available from Montell USA under the trade designations HiFax XL42D01, XL65A01 and XL75A01. The resins were extruded into films using the process conditions in Example 2.

An unfilled dielectric film comprised of the non-crosslinked rubber-modified polypropylene blend, HiFax CA10G of Example 1, was also made into a film using the process conditions of Example 1.

A blend of HiFax XL42D01 and HiFax CA10G was also made into a film using the process conditions of Example 1.

Sheets of the following commercially available dielectric materials were also used in this example: closed-cell crosslinked polyethylene foams available under the trade designations F-CELL and MICROCELL from Sentinel Corporation, continuous modified rubber closed-cell polyolefin blend film available under the trade designation CMR from Sentinel Corporation, and a polymethacrylamide foam available under the trade designation ROHACELL 71 from Rohm Tech, Inc. Samples with dimension 2.75 inch X 2.75 inch (7 cm X 7

cm) were measured for initial dielectric properties at 905 MHz using the procedure specified in Example 1.

Samples of the above materials were submitted for testing in an accelerated test device. This test device is a water cooled xenon arc manufactured by Atlas Electric Devices Co., Model 65WWR or C165, and conforms to standards set forth in ASTM G-26 Type B, BH. The light source is a 6500 watt xenon arc lamp filtered by borosilicate glass filters with a controlled irradiance of 0.35 W/m^2 at 340 nm. A repeating cyclic exposure of 102 minutes light at 63 °C followed by 18 minutes of light plus a water spray was run continuously for the duration of the test.

Dielectric samples were run 1000 hours in this accelerated exposure protocol. Samples were allowed to equilibrate for at least 72 hours at ambient conditions, and dielectric properties at 905 MHz were re-measured according to the procedure of Example 1. The initial and final values of the dielectric constant (ε_r) and loss tangent (tanδ) are shown in Table 4. A comparison of percent change in dielectric constant (ε_r) versus accelerated test exposure time:

{[(exposed - initial)/initial]x 100}

is shown in Fig. 7.

TABLE 4

Dielectric Material	Initial E_r	Initial Tanδ	1000hr E_r	1000hr Tanδ
Montell XL42D01	2.32	0.00265	2.32	0.00000
Montell XL65A01	2.28	0.00295	2.29	0.00065
Montell XL75A01	2.30	0.00240	2.31	0.00050
Montell CA10G	2.23	0.00010	2.21	0.00000
Montell XL42D01/CA10G (1:1)	2.33	0.00010	2.36	0.00030
Sentinel F-Cell XL PE Foam	0.99	0.00170	1.20	0.00000
Sentinel XL PE Foam	0.99	0.00135	1.10	0.00000
Sentinel CMR	1.38	0.00270	1.50	0.00000
Rohm Rohacell 71 Foam	1.20	0.00260	1.45	0.00610

Example 37

Resins may be easily blended with the thermoplastic elastomers of the invention for reasons of cost reduction, performance enhancement, or

processability. In this example some polymers with higher meit flow index, such as Engage 8200 from Dow and Exact 4028 from Exxon, have been added to the thermoplastic elastomers of the invention to provide enhanced processability. The results are shown in Table 5.

In Table 5, HFCA10 is HIFAX CA10G and HFXL42 is HIFAX XL 42D01. Both thermoplastic elastomeric materials are available from Montell USA.

TABLE 5

Sample	ε_r	tan δ
100/0 HFCA10/Dow 8200	2.22	0.00090
75/25 HFCA10/Dow 8200	2.20	0.00083
50/50 HFCA10/Dow 8200	2.18	0.00077
25/75 HFCA10/Dow 8200	2.16	0.00068
1/99 HFCA10/Dow 8200	2.20	0.00052
100/0 HFCA10/Exxon 4028	2.22	0.00090
75/25 HFCA10/Exxon 4028	2.24	0.00082
50/50 HFCA10/Exxon 4028	2.20	0.00070
25/75 HFCA10/Exxon 4028	2.17	0.00067
1/99 HFCA10/Exxon 4028	2.17	0.00050
50/50 HFCA10/HFXL42	2.29	0.00020

The addition of the polymeric fillers to the thermoplastic elastomers of the invention provide a blend with a lower melt flow index. The polymeric fillers act somewhat like a lubricant to enhance processability, and do so without significant alteration of the dielectric properties of the original thermoplastic elastomers.

It will be understood that the exemplary embodiments described herein in no way limit the scope of the invention. Other modifications of the invention will be apparent to those skilled in the art in view of the foregoing description. These descriptions are intended to provide specific examples of embodiments which clearly disclose the present invention. Accordingly, the invention is not limited to the described embodiments or to the use of the specific elements, dimensions, materials or configurations contained therein. All alternative modifications and variations which fall within the spirit and scope of the appended claims are included in the present invention.

What is claimed is:

1. A dielectric material, comprising:

(a) a thermoplastic elastomer with a loss tangent (tan δ) of less than about 0.005; and

(b) a sufficient amount of a filler material to provide predetermined dielectric constant of about 1 to about 50, wherein said filler is a ceramic material comprising at least one of a doped titanate, an un-doped titanate, and mixtures thereof.

2. A dielectric material as claimed in claim 1, further comprising a polymeric filler.

3. A dielectric material as claimed in claim 1, wherein the thermoplastic elastomer has a multi-phase structure comprising:

a thermoplastic polymeric component selected from the group consisting of polypropylene, polyethylene, and copolymers of ethylene and propylene; and

an elastomeric component selected from the group consisting of crosslinked or uncrosslinked butyl rubber, natural rubber, ethylene-propylene rubber (EPR), ethylene-propylene diene rubber (EPDM) and silicone rubber.

4. A dielectric material as claimed in claim 3, wherein the thermoplastic polymeric component comprises at least one of polypropylene and polyethylene, and said elastomeric component comprises at least one of uncrosslinked and crosslinked EPR and EPDM and mixtures thereof.

5. A dielectric material as claimed in claim 3, wherein the thermoplastic component comprises polypropylene and the elastomeric component comprises crosslinked or uncrosslinked EPDM.

6. A laminate structure comprising:

a dielectric substrate comprising a thermoplastic elastomer with a loss tangent (tan δ) of less than about 0.2; and

a metallic layer on at least one side of the substrate.

7. A laminate structure as claimed in claim 6, wherein the thermoplastic elastomer has a loss tangent of less than about 0.003.

8. A laminate structure as claimed in claim 6, wherein the metallic layer is made of a metal selected from the group consisting of gold, silver, aluminum, copper, nickel, tin, chromium and alloys thereof.

9. A laminate structure as claimed in claim 6, wherein the thermoplastic elastomer further comprises a sufficient amount of a filler to provide a predetermined dielectric constant from about 1 to about 50.

10. A laminate structure as claimed in claim 6, wherein the thermoplastic elastomer comprises:

a thermoplastic polymeric component selected from the group consisting of polypropylene, polyethylene, and copolymers of ethylene and propylene; and

an elastomeric component selected from the group consisting of crosslinked and uncrosslinked butyl rubber, natural rubber, ethylene-propylene rubber (EPR), ethylene-propylene diene rubber (EPDM) and silicone rubber.

11. A laminate structure comprising:

a dielectric substrate with a first side and a second side, wherein said substrate comprises a thermoplastic elastomer with a loss tangent (tan δ) of less than about 0.2;

a metallic circuit structure on the first side of the substrate;

a metal layer on the second side of the substrate.

12. A method for tuning the dielectric properties of a dielectric material, comprising the steps of:

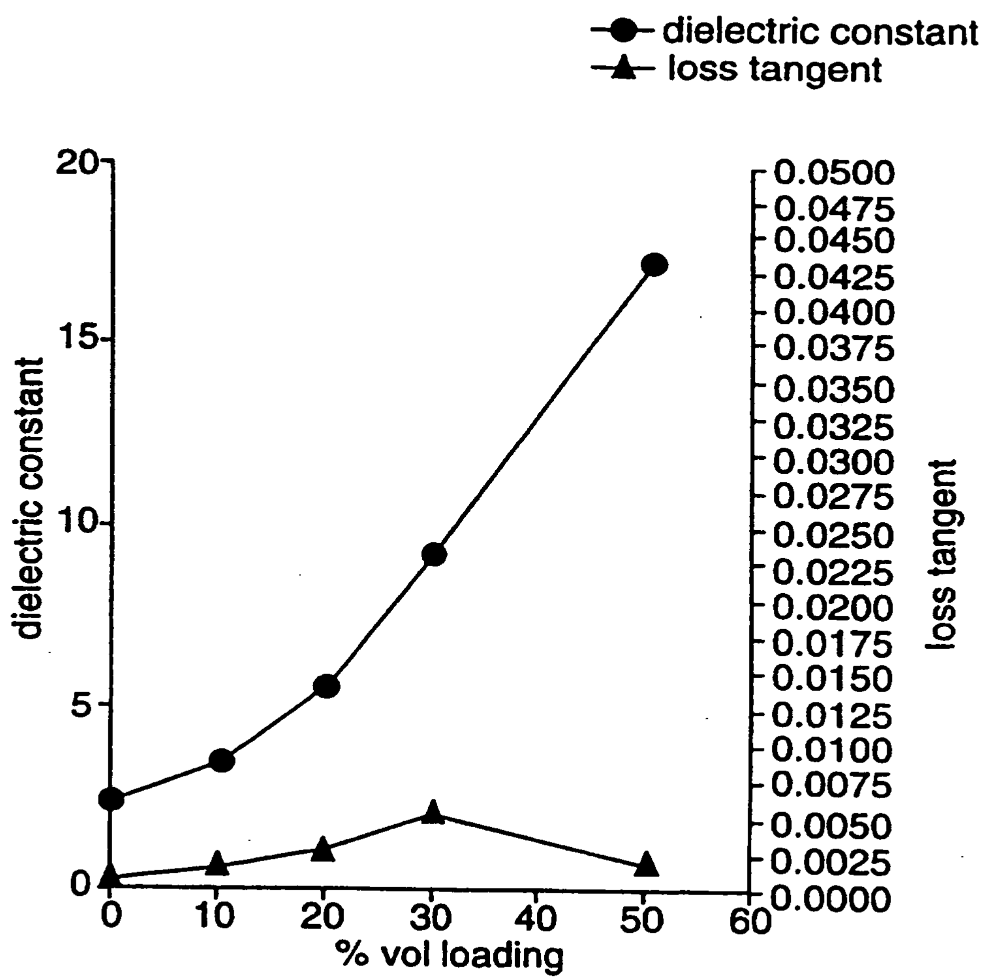
(a) providing a thermoplastic elastomer with a loss tangent (tan δ) of less than about 0.005;

(b) adding to said elastomer a sufficient amount of a filler to provide a predetermined dielectric constant from about 1 to about 50, wherein the filler is selected from the group consisting of ceramics and polymeric materials.

13. A method for making a dielectric laminate, comprising the steps of:

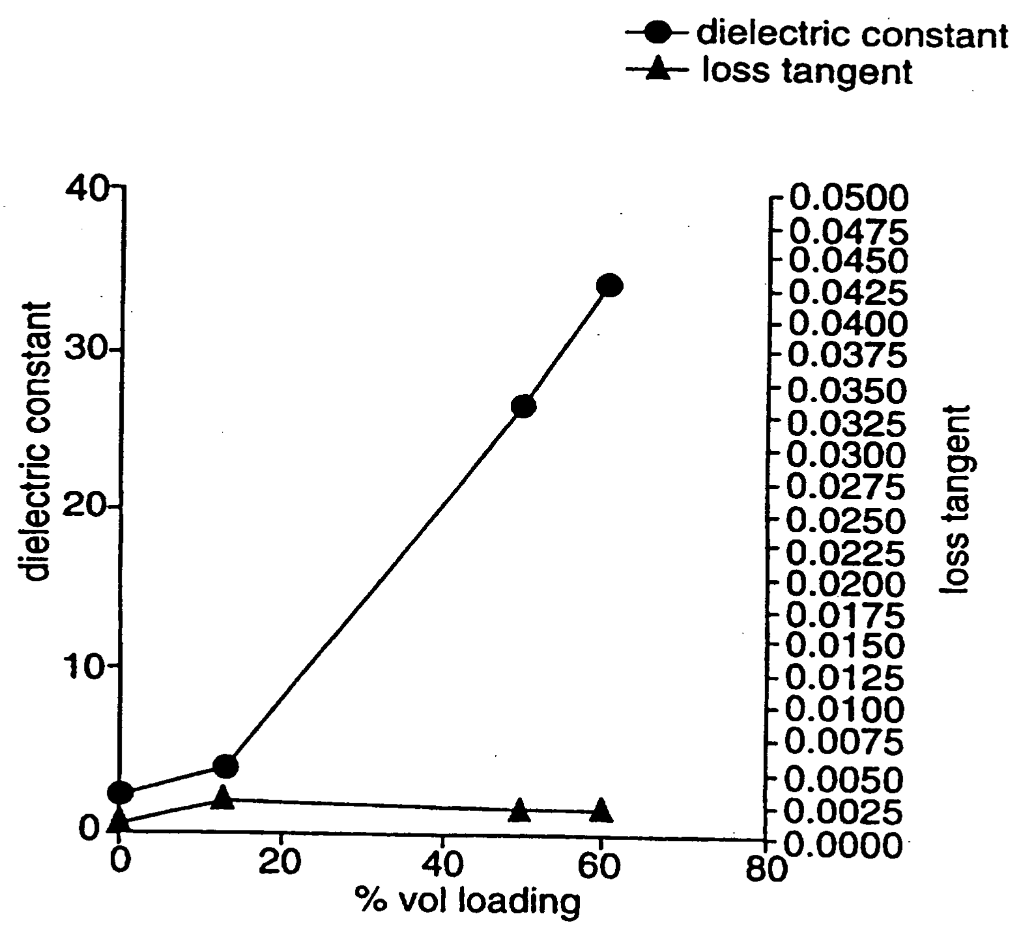
(a) providing a substrate comprising a thermoplastic elastomer with a loss tangent (tan δ) of less than about 0.2;

(b) bonding a metallic layer to at least one side of said substrate.



dielectric constant
loss tangent
20
15
10
5
0
0.0500
0.0475
0.0450
0.0425
0.0400
0.0375
0.0350
0.0325
0.0300
0.0275
0.0250
0.0225
0.0200
0.0175
0.0150
0.0125
0.0100
0.0075
0.0050
0.0025
0.0000
0
10
20
30
40
50
60
% vol loading

Fig. 1


dielectric constant
loss tangent
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30
20
10
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0.0500
0.0475
0.0450
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0.0325
0.0300
0.0275
0.0250
0.0225
0.0200
0.0175
0.0150
0.0125
0.0100
0.0075
0.0050
0.0025
0.0000
0
20
40
60
80
% vol loading

Fig. 2

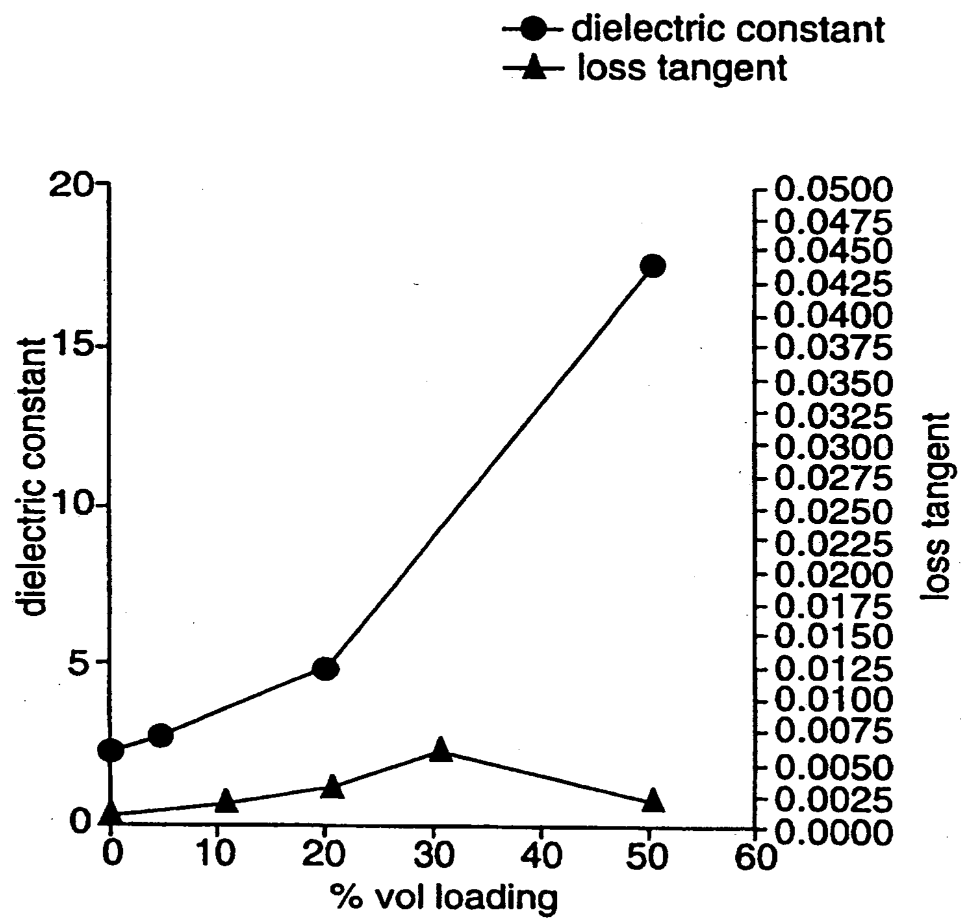
dielectric constant
loss tangent
dielectric constant
loss tangent
20
15
10
5
0
0.0500
0.0475
0.0450
0.0425
0.0400
0.0375
0.0350
0.0325
0.0300
0.0275
0.0250
0.0225
0.0200
0.0175
0.0150
0.0125
0.0100
0.0075
0.0050
0.0025
0.0000
0
10
20
30
40
50
60
% vol loading

Fig. 3

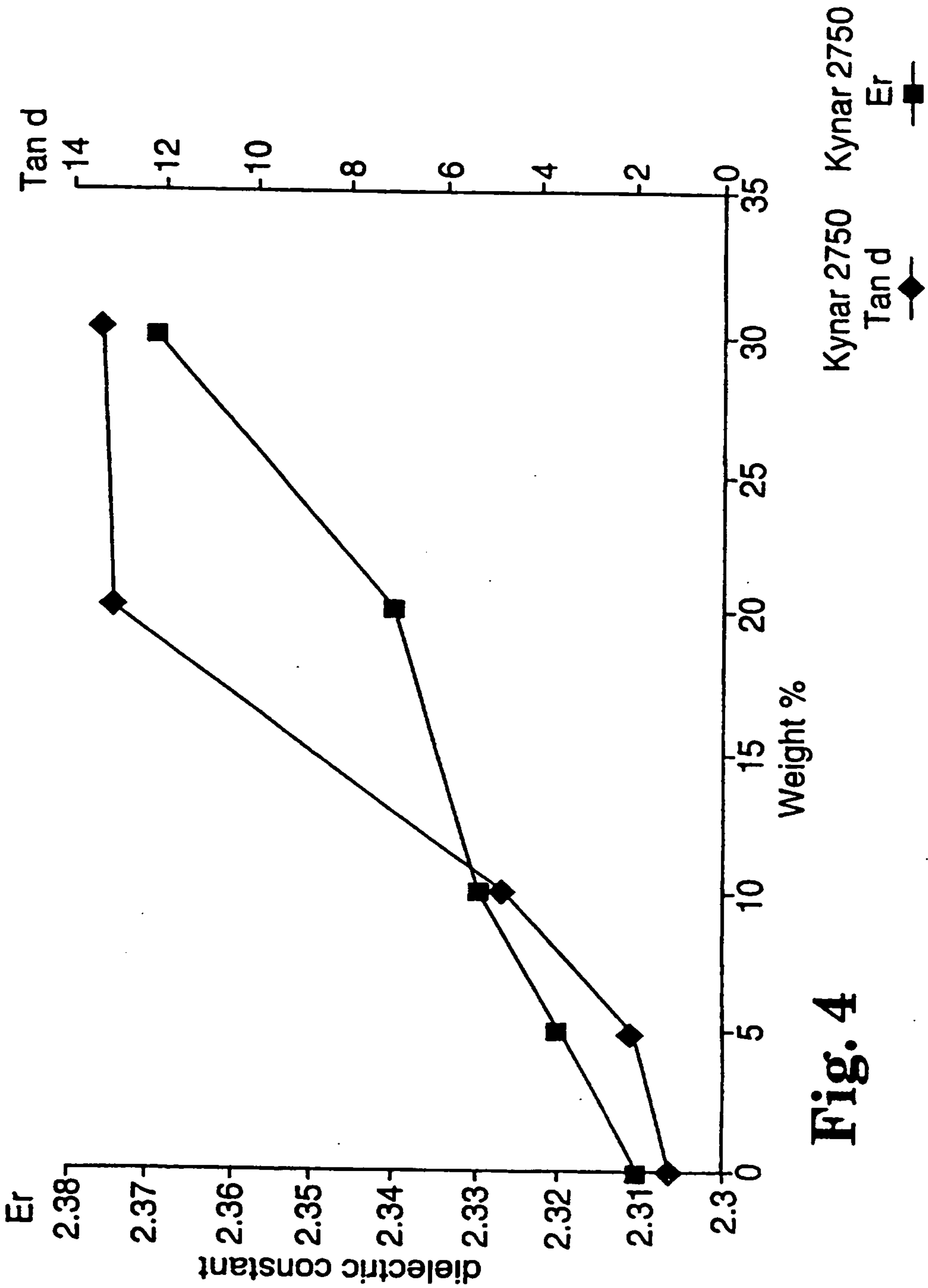
Er
dielectric constant
2.38
2.37
2.36
2.35
2.34
2.33
2.32
2.31
2.3
Tan d
14
12
10
8
6
4
2
0
0
5
10
15
20
25
30
35
Weight %
Kynar 2750 Tan d
Kynar 2750 Er

Fig. 4

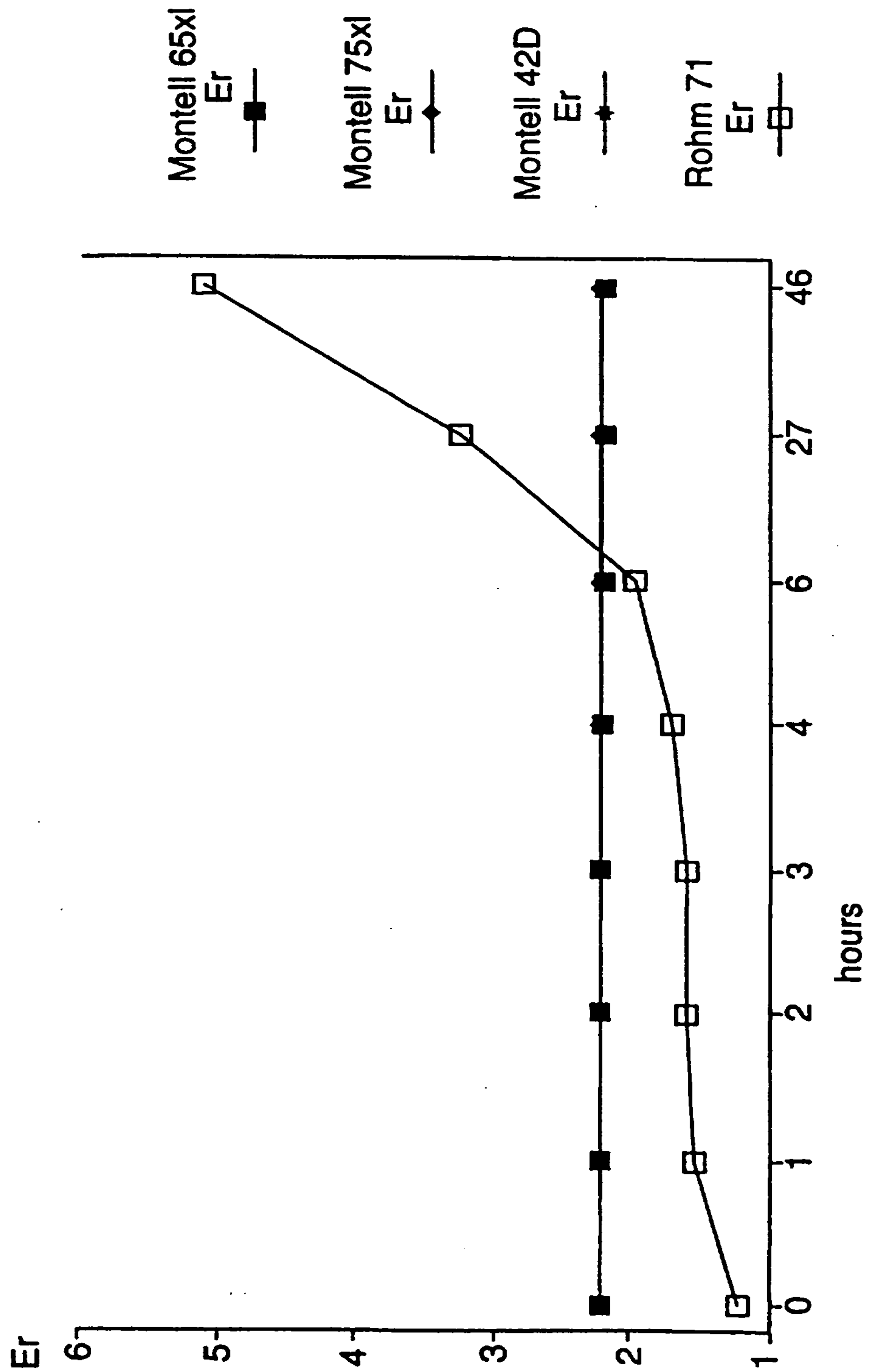
Er
6
5
4
3
2
1
0
1
2
3
4
6
27
46
hours
Montell 65xl Er
Montell 75xl Er
Montell 42D Er
Rohm 71 Er

Fig. 5

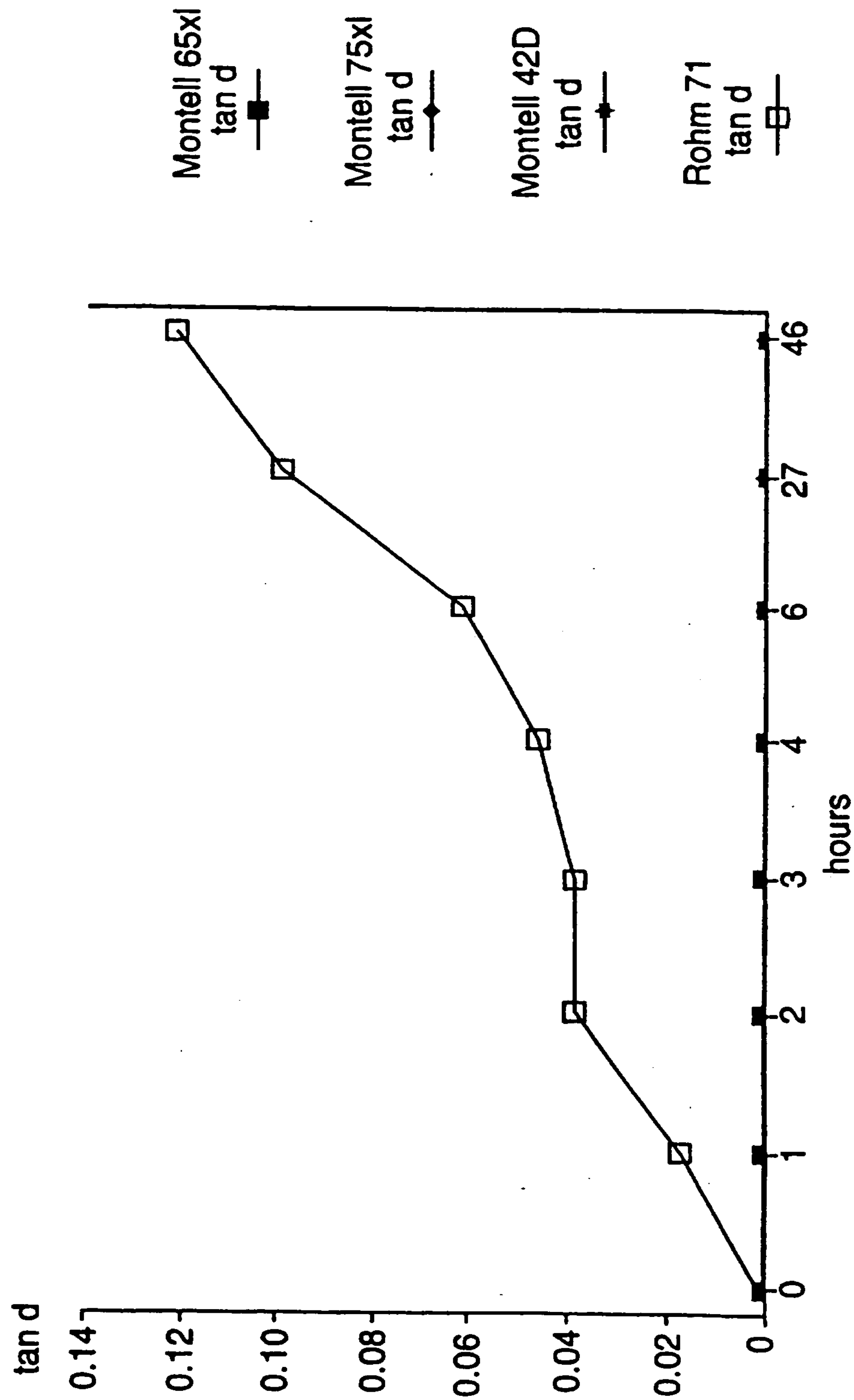
Montell 65xl tan d
Montell 75xl tan d
Montell 42D tan d
Rohm 71 tan d
tan d
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
0
1
2
3
4
6
27
46
hours

Fig. 6

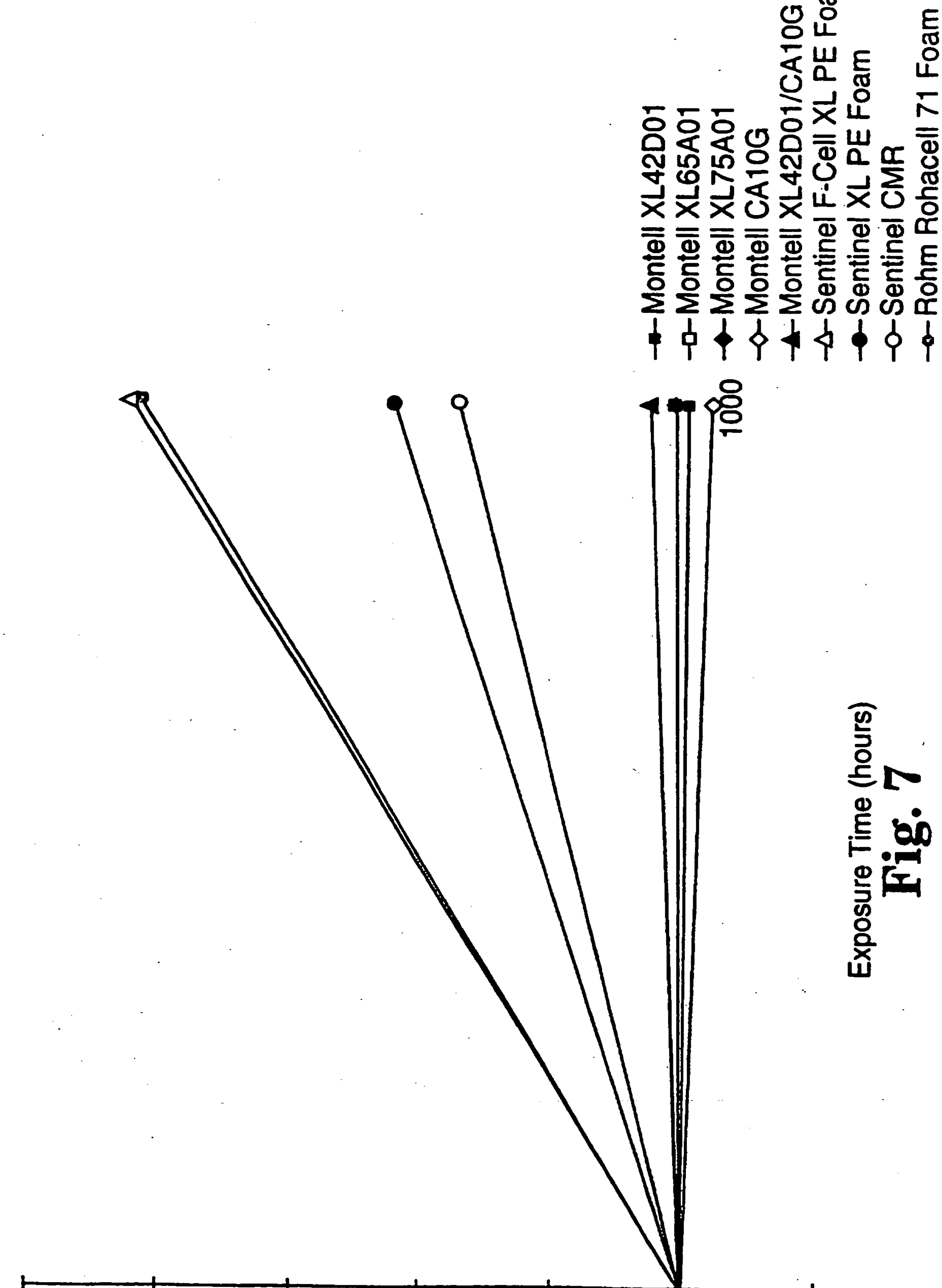
% Change Er
25
20
15
10
5
0
-5
1000
Exposure Time (hours)
Montell XL42D01
Montell XL65A01
Montell XL75A01
Montell CA10G
Montell XL42D01/CA10G (1:1)
Sentinel F-Cell XL PE Foam
Sentinel XL PE Foam
Sentinel CMR
Rohm Rohacell 71 Foam

Fig. 7

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(74) Agents: GWIN, H., Sanders et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

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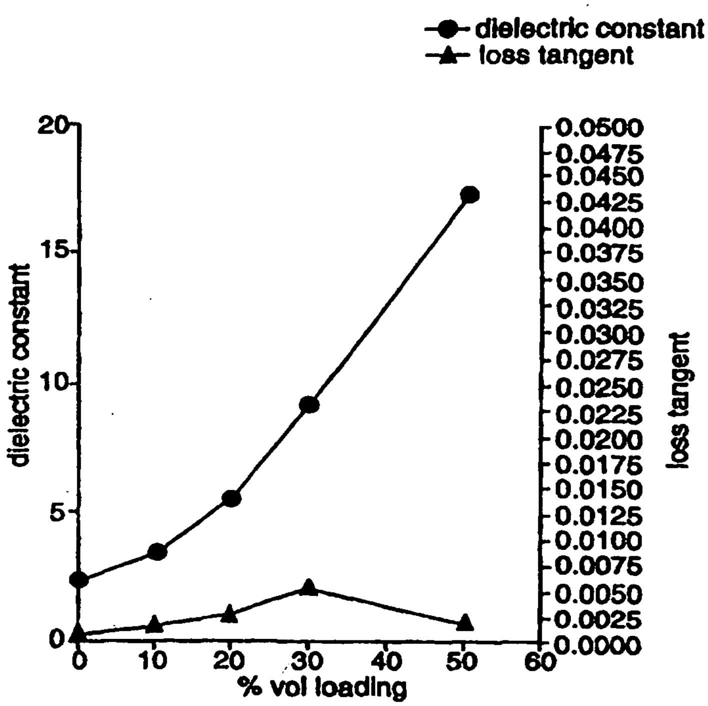
(57) Abstract

A thermoplastic elastomer which may be formulated to have a wide range of dielectric properties as required for a particular application. The material of the invention is preferably provided in the form of a film, which may be bonded to metallic layers, additional dielectric layers, or other circuit structures to form a laminate structure with the desired dielectric properties.



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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 97/01570

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01B3/44 B32B15/08 H05K1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01B B32B H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	FR 2 090 713 A (BASF) 14 January 1972 see page 1, line 1 - line 3; claims 1-4; example 5 ---	
X	FR 2 594 193 A (BRIDGESTONE CORP) 14 August 1987 see page 5, line 1 - page 15, line 7; claims; figure 1 --- -/--	6,13

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 September 1997	23. 10. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	De Jonge, S

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 002, 28 February 1997 & JP 08 258207 A (BRIDGESTONE CORP), 8 October 1996, see abstract	6,13
A	EP 0 398 672 A (MINNESOTA MINING & MFG) 22 November 1990 see column 3, line 12 - line 16; claims	6
A	EP 0 382 557 A (JUNKOSHA CO LTD) 16 August 1990 see page 2, line 48 - line 49 see claims; example 1	6,8-11, 13
A	GB 2 224 464 A (YOKOHAMA RUBBER CO LTD) 9 May 1990 see claims	6,8-11, 13
A	EP 0 243 161 A (YOKOHAMA RUBBER CO LTD) 28 October 1987 see column 2, line 38 - line 55; claims; figure	6,8-11, 13

2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 97/01570

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims 1-5, 12
2. Claims 6-11, 13

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

...ormation on patent family members

Intern al Application No
PCT/US 97/01570

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